Chemistry of Novel Expanded Porphyrins with Main Group Elements(Digest_要約)

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学位論文の要約

Chemistry of Novel Expanded Porphyrins with Main Group Elements

（典型元素を用いた新規な環拡張ポルフィリンの化学）

Chapter 1. General Introduction of Overview of This Thesis

Porphyrin is a well-known organic pigment due to its vital roles in natural systems, such as chlorophyll in photosynthesis. Expanded porphyrins, which have more than five pyrrole subunits, have been extensively investigated for the last two decades because their unique properties. While various metal complexes of expanded porphyrins have been reported so far, their main group complexes have still been limited to a few examples of boron and phosphorus complexes. The author shows that the combination of expanded porphyrins with main group elements is effective to create novel porphyrinoid, such as highly reduced expanded porphyrins and Möbius antiaromatic molecule.

Chapter 2. Phosphorus Complexes of Triply Fused Pentaphyrins

The treatment of *meso*-aryl-substituted [24]pentaphyrin with $POCl_3$ gave the P=O complex having a triply fused macrocycles the *N*-fusion reaction and C–C bond formation between the pyrrolic β-positions. The P=O complex was converted to the P=S complex by the action of Lawesson's reagent, while the P=O complex was converted to the P–BH_3 complex with $BH_3{\cdot}SMe_2$ with the concomitant hydrogenation at the pyrrolic β-position. The treatment of P–BH_3 complex with triethylamine provided P=O complex of chlorin-type pentaphyrin, which has same macrocyclic structure as P–BH_3. The P–BH_3 complex is the first phosphorus(III) complex of porphyrinoid. The P=O and P=S complexes exhibit stron 24π antiaromatic character due to their highly rigid structure. On the other hand, P–BH_3 and P=O complexes of chlorin-type pentaphyrin are nonaromatic macrocycles due to the weak maclocyclic π-conjugation.

Chapter 3. Möbius Antiaromatic and Hückel Aromatic Phosphorus Complexes of [34]Heptaphyrins

Phosphorus insertion into *meso*-pentafluorophenyl [32]heptaphyrin provided doubly twisted Hückel aromatic [34]heptaphyrin as a sole product. On the other hand, singly twisted Möbius antiaromatic [34]heptaphyrin and doubly twisted Hückel aromatic [34]heptaphyrin were formed in the phosphorus insertion reaction to *meso*-2,6-dichlorophenyl [32]heptaphyrin. Möbius antiaromatic character has been confirmed on the basis of the X-ray structure, a weak paratropic ring current, ill-defined absorption characteristics, fast excited-state decay, and a relatively small TPA cross section. In aliphatic nitrile solutions, Möbius antiaromatic complex underwent

the quantitative thermal isomerization of P=O moiety to produce more stable Hückel aromatic complex with the concurrent molecular topology switch, hence indicating the Möbius antiaromatic complex to be a kinetically controlled species as a rare case.

Chapter 4. Synthesis of 2,3,17,18-Tetraethylsulfanyl[30]hexaphyrin as the First Aromatic Expanded Isophlorin Free-base

The author prepared tetraethylsulfanyl [28]hexaphyrin, which was converted to tetraethylsulfonyl [28] hexaphyrin by the oxidation with mCPBA and to tetraethylsulfanyl [26]hexaphyrin by the oxidation with MnO_2. While [28]hexaphyrins are antiaromatic molecules exhibiting paratropic ring current and figure-of-eight conformations, the major conformer of [26]hexaphyrin in $CDCl_3$ solution is an aromatic species that displays a diatropic ring current around the rectangular shape. The reduction of tetraethylsulfanyl [28]hexaphyrin with excess amount of $NaBH_4$ produced tetraethylsulfanyl [30]hexaphyrin as the first example of aromatic free-base expanded isophlorin. This highly reduced oxidation state is likely stabilized by the four β-ethylsulfanyl substituents.

Chapter 5. Synthesis of 2,3,17,18-Tetrahalogenated Hexaphyrins and the First Expanded Phlorins

The author established the convenient synthesis of *N*-protected 3,4-dichloro- and 3,4-difluoropyrrole from *N*-protected 3,4-dibromopyrrole. 3,4-Dihalopyrroles were condensed with dipyrromethane dicarbinol to produce 2,3,17,18-tetrahalo[26]hexaphyrins and [28]hexaphyrins. These 2,3,17,18-tetrahalogenated hexaphyrins display variable structural and electronic properties depending upon the β-substituted halogen atom and the number of π-electrons. [28]Hexaphyrins were further reduced with a large excess $NaBH_4$ to provide *meso*-hydro-hexaphyrins. Their spectral, structural and electrochemical properties indicate that they are the first examples of phlorin-type hexaphyrins in the literature.

Chapter 6. Distinct Möbius Aromatic [28]Hexaphyrin Free-base with Rigid Carbon Bridges

The author found that reaction of [28]hexaphyrin with triethylamine in the presence of $SiCl_4$ under O_2 atmosphere provided a new Möbius aromatic [28]hexaphyrin free-base with highly rigid structure. While the mechanism is still unknown, reaction with radical species is most likely pathway. Since radical reaction of expanded porphyrins has not been reported so far, analysis of this reaction mechanism should be disclose the reactivity of expanded porphyrins toward radical species. Furthermore, this [28]hexaphyrin free-base can provide new insight about Möbius aromatic molecules without transition metals.